6. WINTER MEASUREMENT PROGRAM

The winter measurement program was designed to understand the detailed causes of primary and secondary components of $PM_{2.5}$ during pollution buildup episodes and to apply and evaluate state-of-the-art air quality models. The winter study was conducted over a two month period from December 1, 2000 to February 3, 2001. This section specifies the variables measured, averaging times, sampling and analysis frequencies, monitoring systems, and sampling sites that supplemented those operated during the annual average study. The network description tables in this section show the types of measurements that were added during winter. The last part of this section describes how these additional data will be used to expand on the data uses specified in Section 5 to attain each CRPAQS objective.

In addition to continuous air quality measurements over the two month period, four episodes of three to four-day duration, for a total fifteen days, were selected according to a forecast of PM buildup. Detailed filter-based chemical measurements and fog measurements were conducted during each episode. The dates of these episodes were:

December 15 through 18, 2000

December 26 through 28, 2000

January 4 through 7, 2001

January 31 through February 3, 2001

6.1 CRPAQS Winter Aerosol Measurements

As noted in Section 4, several sites were upgraded to anchor sites for the winter campaign and additional instrumentation was added to the annual average anchor sites. Nephelometers were also added at 15 satellite sites for the winter study period. Table 6.1-1 specifies the instruments that were operated continuously at each of these sites throughout the two month winter period. The table lists sites for which instruments were added for the winter period, as well as those sites which had continuous measurements for the entire annual period, including the winter. The continuous monitors were operated every day, throughout the day, over the two month winter period. Further details regarding the winter measurements, including diurnal sampling schedules, are shown in Tables A-1 through A-3 in Appendix A.

High sensitivity sulfur dioxide was monitored only at the Bakersfield site to examine correspondence of SO_2 pulses with sulfate pulses that might arise from nearby oilfield operations. The original Study Plan called for hydrogen peroxide and radicals to be measured at Angiola, as this site is distant from the very reactive but spatially non-representative species anticipated near source emissions in cities. However, it was judged that the expense and uncertainty of these measurements did not merit their use. Model input requirements can be met satisfactorily by using typical values for the region, as determined from prior studies.

Detailed filter-based chemical measurements and fog measurements, as described in Table 6.1-2, were acquired during four intensive operating periods consisting of $PM_{2.5}$ episodes of three to four days duration each. Monitoring during these episodes was initiated by a forecast team that had refined and tested the forecast methodology during the two prior winters. In addition to these special episodic measurements, all of the annual study filter measurements took place at the six day intervals specified in Section 5 throughout the winter study period.

Filter samples were taken throughout each episode to characterize organic and inorganic chemistry. The diurnal sampling periods were selected to encompass periods during which emissions and meteorology have been observed to change. The morning rush hour period was represented by a sample collected between 0500 and 1000 PST. Rapid changes in vertical mixing between 1000 and 1300 PST were represented by a single sample, as was the afternoon period from 1300 to 1600 when vertical mixing is believed to be most vigorous. Organic compounds require more sample than do inorganic compounds, so these two periods were combined for a single 1000-1600 sample for organics. Samples collected from 1600-2400 and 0000-0500 characterized the overnight period. An exception to this schedule was made for the PUF/XAD particulate organic measurements. Whereas four samples were collected on each episode day at the urban Fresno-First Street site, only two samples were collected each day at the outlying sites (Angiola, Bethel Island, and Sierra Nevada Foothills). These longer sampling periods were adopted to account for the lower ambient particulate organic concentrations at the rural sites, and also to conserve funding for these very expensive analyses.

The satellite sites operated with a single 24-hour Minivol sample every day during each episode. Also, nephelometers were added at fifteen satellite sites for the winters. These nephelometers had been used in the fall network around Corcoran, and were moved to satellite sites in late November 2000 when the fall study was complete.

6.2 Winter Meteorological Measurements

The annual meteorological network operated throughout the winter study period. Additional doppler sodar wind monitors were added to the annual network to better characterize transport and mixing aloft. Additional radar profilers were also deployed during the CCOS summer 2000 study and remained through the CRPAQS winter intensive study at Chico, Waterford, Fresno Air Terminal, and San Martin.

In addition, the remote sensors of upper air winds and temperature were supplemented with rawinsondes launched four times per day at Bakersfield and Fresno on each of the fifteen winter episode days. Also, the schedule of routine launches at Oakland was augmented to four launches per day (0400, 1000, 1600, and 2200 PST) on the fifteen episode days, rather than the normal two launches per day. These rawinsondes provided continuous relative humidity measurements as well as more detailed wind measurements in the mixed layers.

6.3 Tower Measurements

In addition to the meteorological, light scattering, and particle size measurements acquired during the annual program, a number of continuous measurements were added to the Angiola tower for the two-month winter campaign. A nephelometer was added at the base of the tower to provide, along with existing nephelometers at the midpoint and top of the tower, a measure of the vertical gradient of light scattering. At the top of the tower, instruments were added to measure light absorption, NO_y, O_3, and $PM_{2.5}$ nitrate. Fog chemistry measurements at several levels on the tower were also added for the winter. The Walnut Grove tower was also instrumented with nephelometers, aethalometers, and continuous nitrate analyzers at the 10 m and 260 m levels. These tower measurements allowed detailed examination of vertical pollutant transfer between the surface layer and the valleywide layer to test the hypothesis that vertical mixing and non-afternoon transport above the surface layer mixes pollutants from different sources. From ~1700 to 1000 PST the next day, the tower measurements were designed to estimate concentrations above the surface layer, but below the top of the valleywide layer.

6.4 Winter Special Studies

Two special studies were conducted during the two month winter period.

1) A single particle quantification experiment was designed to examine individual particles to determine their formation mechanisms and sources. Time of flight mass spectrometers were deployed at the Fresno and Angiola sites to quantify the composition and size of individual particles. MOUDI particle size samples accompanied the single particle measurements at both sites on the 15 episode monitoring days.

2) Fog characterization experiments were conducted to understand the extent to which fog attenuates $PM_{2.5}$ concentrations by occult deposition. Quantity and composition of fog that deposits to the surface were measured at Angiola, as were fog composition in fog droplets of different sizes at different levels of the micrometeorological tower. Less detailed measurements were taken at three outlying sites (Bakersfield-California Avenue, Helm, and a special winter-only site at McKittrick) when fog was present to obtain a horizontal distribution.

The original study plan called for additional winter special studies using aircraft and/or balloon measurements to evaluate the variability of depth in the valleywide layer and to evaluate the changes in concentration of secondary aerosol and precursors with height. These airborne measurements were never implemented because the days of most interest for measurements would be too foggy and/or hazy to allow safe flying conditions. Also, it was judged that the value of the data did not merit the high cost of the flights, and that the funding could be put to better use in ground-based measurements.

6.5 Uses of Winter Study Measurements to Attain Objectives

The following sub-sections briefly describe how the Winter study data will be used to accomplish each of the CRPAQS field study objectives specified in Section 1.

6.5.1 Winter Study Objective 1: Quality Data Base

Performance tests, quality audits, and measurement comparisons will be used to evaluate the accuracy, precision, validity, and completeness of the CRPAQS Winter study database. Winter conditions are harsher than other times of the year, with substantial fog and rain that will challenge sampler reliability. The particles being sampled are also more labile, containing larger amounts of liquid water, ammonium nitrate, and volatile organic carbon from wood combustion. The contrast of instrument performance during winter with that for other seasons will reveal how accuracy and precision can differ with environmental conditions. Additional comparisons of continuous and filter measurements will be made for nitrate and sulfate.

6.5.2 Winter Study Objective 2: Evaluate Backbone Network

Sulfate and nitrate concentrations measured using the continuous analyzers deployed at anchor sites during the winter will be examined for short pulses of $PM_{2.5}$ that can be attributed to nearby intermittent emissions or to small and short-duration changes in wind direction. The correspondence of sulfur dioxide with sulfate at the Bakersfield site will likely represent contributions from nearby sources that can be separated from more regional contributions.

The spatial variability of $PM_{2.5}$ concentrations will also be evaluated for $PM_{2.5}$ and specific chemical components for different meteorological and emissions situations. The large array of gradient sites will allow the presumption of secondary aerosol spatial uniformity to be evaluated throughout the region.

6.5.3 Winter Study Objective 3: Temporal and Spatial Distributions

Diurnal, weekly, and seasonal variability are likely to be different during winter than during other parts of the year when surface flows are better defined and more consistent. Changes in primary and secondary aerosol concentrations with time of day will be given attention to determine consistency or inconsistency with the hypothesis of afternoon mixing as the main dilution mechanism for primary particles and the main augmentation mechanism for secondary particles. Measurements from the Sierra Foothills and 100 m tower will be examined over the morning layer coupling transition and as the valleywide layer top passes through the Sierra Foothills monitors.

6.5.4 Winter Study Objective 4: Boundary Layer and Regional Circulation

Horizontal winds from profilers, sodars and surface stations at various elevations above ground level will be examined for different times of the day, week, season and year. Wind directions, speeds, and potential transport distances within the surface layer and between the top of the surface layer and top of the valleywide layer will be examined to

determine how long pollutants might reside aloft and how far they might travel. This will be examined for interbasin transport pathways, especially between the Bay area and the SJV and between the Sacramento Valley and the SJV.

Variations in the timing and extent of vertical mixing between the surface layer and the valleywide layer will be determined for episodes. The vertical and horizontal extent of fogs will be examined from a combination of RH, nephelometer, ASOS, and NWS observations. Upward movement of particles owing to heat buoyancy and turbulence will be balanced against downward movements owing to heat and momentum transfer as well as gravitational settling for fog and non-fog situations to evaluate particle growth in fog as a major deposition mechanism. Dispersion under low wind speed conditions will be elucidated for better customization of dispersion models. Specific values for dispersion parameters will be estimated from tower turbulence measurements for each monitored layer and time of day.

The frequency, duration, spatial extent, and intensity of meteorological variables that affect pollution will be different from winter as compared to other seasons. Exceptions to these hypotheses will be sought: 1) temperatures and relative humidities favor particulate ammonium nitrate; 2) insolation is insufficient to affect photochemical transformations near the surface and most of this takes place near the top of the valleywide layer; 3) storms effectively reduce particle concentrations to low levels; and 5) fogs and low clouds enhance secondary aerosol formation more than they remove it during $PM_{2.5}$ buildup episodes.

Meteorological models will be applied to the profiler, RASS, and tower measurements. These measurements will serve as model inputs and to evaluate the accuracy and validity of the model formulations.

6.5.5 Winter Study Objective 5: Source Zones of Influence and Contributions

$PM_{2.5}$ chemical measurements will be used with the CMB model to estimate primary source contributions to ambient concentrations for individual samples and annual averages. The CMB will use all gaseous and particulate organic and inorganic speciation data for the diurnal sampling periods. In addition to quantifying primary source contributions, the CMB analysis will determine differences between primary emissions profiles and ambient concentrations consistent with, and at odds with, secondary aerosol formation. The organic compound measurements at the anchor sites will permit the distinction of diesel, cold start, high emitter, and hot stabilized vehicle exhaust, wood burning, cooking, and other organic carbon sources to be distinguished by time of day. The afternoon samples will quantify these urban-generated contributions that reach non-urban areas and presumably reach other urban areas via the vertical mixing and valleywide layer transport pathway.

Outputs from the wind models will be used in transport and transformation models to determine which source areas or specific sources could have made negligible, minor, moderate, large, or major contributions at each receptor. More careful attention to transport in the surface and valleywide layers will be needed in these models. Source contribution

estimates at different locations will be compared to determine their consistency with emissions inventories and modeled zones of influence.

6.5.6 Winter Study Objective 6: Secondary Aerosol Sources

Aerosol equilibrium models will be applied to the continuous sulfate, nitrate, and nitric acid measurements to verify the hypothesis that there is sufficient ammonia to completely neutralize available acid throughout each day of each episode.

Organic gaseous precursors and particle organic compounds will be examined for changes in abundances that indicate secondary aerosol formation

6.5.7 Winter Study Objective 7: Conceptual Model Refinement

Wintertime flows at the surface, within the valleywide layer, and above the layer will be established for different synoptic conditions. These are currently unknown. The vertical mixing with reaction and transport aloft hypothesis in Section 3 will be tested. This is crucial to understanding the effect of one urban area's emissions on pollution levels on other central California urban areas during winter, especially for secondary aerosol components.

6.5.8 Winter Study Objective 8: Simulation Methods

Full-scale application of the most advanced emissions, meteorological, and air quality models will be applied to the winter episodes. The winter measurements will supply initial and boundary conditions as model inputs. They will supply parameters for deposition and dispersion. They will supply substantial data for comparison with model outputs in order to evaluate which components of the models are not representing the physical and chemical processes that occur during winter in central California.